IMMOBILIZATION OF RADIUM IN URANIUM MINE AND MILL TAILINGS

Final Report

Nova Scotia Research Foundation Corporation
Dartmouth, Nova Scotia

IMMOBILIZATION OF RADIUM IN URANIUM MINE AND MILL TAILINGS

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by

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Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

MICROMEDIA
MAY 13 1983

DSS FILE NUMBER	:	17SQ.23440-0-9094
DSS CONTRACT SERIAL NUMBER	:	1SQ80-00160
CANMET PROJECT NUMBER	:	23440 (UP-N-90)
CANMET SCIENTIFIC AUTHORITY	:	Dr. J. Skeaff

52 pp

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23 February, 1982.

Dr. J. Skeaff
Department of Energy, Mines & Resources
CANMET, Mineral Sciences Laboratory
555 Booth Street
Ottawa, Ontario
K1A OG1.

Dear Dr. Skeaff:

In your hands is the report pertaining to the application of arsenate to the immobilization of radium in uranium mine and mill tailings. You should note that the results are not related too well to the theory as this work was terminated too soon.

I feel this research was terminated too early leaving the question of conditions for the maximum effectiveness of radium removal and containment unanswered. Early termination also prevented the study of column regeneration and radium recovery.

We had agreed that you would supply me with samples of tailings for testing, in view of the fact that I never received these samples work on Phase 3 of this project was impossible. You should appreciate that the experiments in Phase 3 would require time due to the slow perculation of the aqueous phase through the exchanger beds. These experiments should have overlapped the experiments in Phases 1 and 2.

I bring to your attention that thorium and arsenate appear to react in acid solutions. Further work is thus indicated with regard to this reaction. Thorium's reaction with arsenate is similar to the reactions of the rare earths with regard to acidity.

I take this opportunity to express my appreciation for the opportunity to carry out this work and hope that in the future we may pursue answers to other questions.

Yours truly,

Gerald D. Lutwick

Gerald B. Lutwick, Head
Analytical Section
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GDL/rtc

Telex 019-22719

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ACKNOWLEDGMENT

The author and the Nova Scotia Research Foundation Corporation thanks the Department of Supply and Services and the Department of Energy, Mines and Resources for financing this research project.

SUMMARY

Radium has been coprecipitated from solution as the arsenate in which ferric iron, barium, copper and lead are the macro ions. The order of efficiency of the macro ions in removing radium was found to be Ba > Fe > Pb > Cu at a pH of 6. It is expected that at higher pH's ie.e. great than 8 ferric iron will change positions. This change in position will be caused by the formation of ferrate ion hence increasing the solubility of ferric arsenate.

The removal of radium from solution by ion exchangers consisting of the arsenates of ferric iron, barium, copper and lead was successful. As the pH is increased from 4 to 10 the efficiency of these exchangers in removing radium increases. The columns removed over 99% of the radium at pH's of 5.6 and higher. The order of efficiency of the exchangers in removing radium is not well defined.

Thorium has been precipitated as the arsenate over the pH range of 2 to 9.6. This reaction suggests the possibility of using arsenate to remove thorium from uranium mill plant streams and as a reagent to keep thorium in the tailings ponds.

IMMOBILIZATION OF RADIUM IN URANIUM MINE AND MILL TAILINGS

Uranium has been mined in Canada since 1943. Since 1948 there was an increase in the number of producing mines and mills most of which closed down in the early 1960s. The recent increase in demand for uranium has stimulated a rejuvenation of the uranium industry with the opening of new mines and mills and the reopening of old mines and mills. Since uranium ores contain from 0.1 to 0.3% U_3O_8, 99.8% of the ore is discharged as waste which contains all the radioactive daughters of uranium. It is anticipated that by the year 2000, 300 million tonnes (Cherry) will have been produced of which the total annual radioactivity disposed of as railings will be comprised of 9×10^3 Ci of Ra^{226}, 6×10^3 Ci Th^{230} and 2×10^3 Ci Pb^{210}. Mining and milling activity will thus free for migration large quantities of radioactivity. Free to migrate, these radioactive elements can enter the environment and thus the food chains by ground and rain water leaching of tailing dumps.

The confinement of radioactive wastes was given little attention by the mill operators until 1965 at which time the treatment of effluent waters to reduce radium^{226} was inaugerated. Previous to this time mill effluent was discharged to a tailings basin in which the solids settled to the bottom.

Tailings from uranium mills are usually received and impounded in natural depressions in the land adjacent to the mills. At least two tailing ponds are used. The first pond allows for the

settling out of sand, silt and clay particulate matter. The effluent from this pond is treated with barium chloride to effect reduction of dissolved radium after which the effluent enters the second pond. In the second pond the barium-radium sulphates settle to the bottom and the effluent is released to the environment. The Provinces, Saskatchewan and Ontario, have set a maximum permissible Concentration for ^{226}Ra in drinking water of 3 pCi/L.(Cherry). The Atomic Energy Control Board and the Canada Department of the Environment have proposed a target of 10 pCi/L as a limit for ^{226}Ra in effluents from tailings pond.

The tailings problem considered in this paper is addressed to containing the radionuclides in the tailing ponds and removing the radionuclides in plant streams. Active and inactive uranium-mill tailings areas are in part saturated under positive pore-water pressure, i.e., a water table occurs in the tailings[1] (Cherry). Considering that the water table is in equilibrium, averaged over a period of time, then the quantity of water entering the tailings zone equals the quantity of water leaving the tailings zone. The water leaving the tailings zone will be contaminated with minerals from the tailings hence contaminating the waters adjacent to the tailings. With time the area of contamination increases until finally the contaminants enter the rivers and lakes and then the biosphere. Subsurface water can enter the soil zone and thus carry contaminants to the vegetation.

Contaminant migration by groundwater paths can be prevented by covering the bottom of the tailings pond with an impermeable blanket. Such a blanket requires covering the area with the same material before

abandonment, otherwise the tailings would become saturated with rain and snowmelt followed by surface run off. The surface runoff would carry contaminants, both dissolved and particulate, into the adjacent areas.

The reduction of solubility of radium and hence the quantity entering the biosphere requires the formation of an insoluble salt and stabilizing the conditions of the tailings ponds to keep solubility at a minimum. The latter involves pH control hence the addition of a mineral such as limestone to the tailings. The limestone, with time, will be consumed hence the conditions of the tailings returns to its original condition. This return to the polluting conditions will be enhanced by acid rains.

The formation of a highly insoluble salt by the pollutants offers a lasting solution to the radionuclide pollution problem. The salt, to be beneficial, should be highly insoluble over an extended pH range, especially on the acid side of neutrality. The chemistry of radium is very similar to the chemistry of barium thus since barium forms an arsenate more insolbule than the sulfate, radium is expected to form an arsenate which is more insoluble than the radium sulfate. Accordingly arsenate should be a better reagent than sulfate in treating uranium mill effluents and tailings ponds in preventing radium pollution of the environment.

SOLVATION OF SALTS

General Theory

Dissolution of anionic compound can be depicted as the separation of the anion and cation of which the compound is composed in a solvent. The cation and the anion

$$M_m S_n = mM + nX \quad (1)$$

interact with the solvent to form complexes and/or new ions or other compounds. In an aqueous solution, the "cation forms aquated ions which may undergo successive deprontonation of the aqueous complex as in reactions (2), (3) and (4).

$$M(H_2O)_n = M(H_2O)_{n-1}\ (OH)^- + H^+ \quad (2)$$

$$M(H_2O)_{n-1}\ (OH)^- = M(H_2O)_{n-2}\ (OH)_2^{-2} + H^+ \quad (3)$$

$$M(H_2O)_{n-2}\ (OH)_2^{-2} = M(H_2O)_{n-3}\ (OH)_3^{-3} + H^+ \quad (4)$$

Successive deprotonation occurs in the precipitation of ferric hydroxide from aqueous solution. Consider an aqueous solution, pH less than 2 containing ferric iron, the ferric iron exists in the solution as the hexahydrate, $Fe(H_2O)_6^{+3}$). Increasing the pH by the addition of a base initiates deprotonation as in reaction 5.

$$Fe(H_2O)_6^{+3} + OH^- \rightarrow Fe(H_2O)_5\ (OH)^{+2} + H_2O \quad (5)$$

A second proton is released, as in reaction 6, when the pH is increased further followed

$$Fe(H_2O)_5\ (OH)^{+2} + OH^- \rightarrow Fe(H_2O)_4\ (OH)_2^+ + H_2O \quad (6)$$

by the formation of a precipitate ferric hydroxide.

$$Fe(H_2O)_4(OH)_2^+ + OH^- \rightarrow Fe(H_2O)_3(OH)_3 + H_2O \quad (7)$$

The anion may similarly undergo hydrolysis to form protonated anion species as in reactions (8), (9) and (10).

$$X + H_2O = XH + OH^- \quad (8)$$

$$XH + H_2O = XH_2 + OH^- \quad (9)$$

$$XH_2 + H_2O = XH_3 + OH^- \quad (10)$$

All reactions depicted involve equilibria hence the dissolution of an ionizing compound involves satisfying the solubility product (Ksp) of the compound and the various equilibria involved with the interaction of the ions with the solvent.

The interaction of the ions with the solvent increases the solubility of the compound to a value greater than that calculated from the solubility product without considering solvolysis. Considering solvolysis the total concentration of anion S_x and cation S_m, in solution is depicted by equation (11) and (12)

$$S_x = X + XH + SH_2 + \text{etc.} \quad (11)$$

$$S_m = M + MOH + M(OH)_2 + \text{etc.} \quad (12)$$

Substituting into equations (11) and (12) the various equilibrium expressions in terms of X and M equations (13) and (14) are obtained.

$$S_x = X + \frac{K_{x1}X}{(OH)} + \frac{K_{x1}K_{x2}}{(OH)^2}X + \text{etc.} \quad (13)$$

$$S_m = M + \frac{K_{m1}}{(H+)}M + \frac{K_{m1}K_{m2}}{(H^+)^2}M + \text{etc.} \quad (14)$$

Removing X and M and letting the products of the equilibria constants be represented as β, equations (15) and (16) are obtained which expresses the concentrations

$$S_x = X \left[1 + \frac{\beta_1}{\{OH\}} + \frac{\beta_2}{\{OH\}^2} + \text{etc.}\right] \quad (15)$$

$$S_m = M \left[1 + \frac{\beta_1}{\{H^+\}} + \frac{\beta_2}{\{H^+\}^2} + \text{etc.}\right] \quad (16)$$

of the anion and cation in terms of the total concentrations, equilibrium constants and acidity. Substituting these values, in which

$$X = S_x/\left[1 + \frac{\beta_1}{\{OH\}} + \frac{\beta_2}{\{OH\}^2} + \text{etc.}\right] \quad (17)$$

$$M = S_m/\left[1 + \frac{\beta_1}{\{H^+\}} + \frac{\beta_2}{\{OH\}^2} + \text{etc.}\right] \quad (18)$$

into the expression for the solubility product an expression for total solubility is obtained

$$K_{sp} = \{M\}^m \{X\}^n$$

$$K_{sp} = \{S_x\}^n \{S_m\}^m/\left[1 + \frac{\beta_1}{\{OH\}} + \frac{\beta_2}{\{OH\}^2} +\right]^n \left[1 + \frac{\beta^1}{\{OH\}} + \frac{\beta^2}{\{OH\}^2} +\right]^m \quad (19)$$

Letting the expressions in the denominator of equation (19) be represented by Σ_x and Σ_m equation (20) is obtained. Equation (20)

$$K_{sp} = \{S_x\}^n \{S_m\}^m/\Sigma_x^n \Sigma_m^m \quad (20)$$

can be rearranged to express the total concentration of anion or cation. These

$$S_x = (K_{sp} \Sigma_x^n \Sigma_m^m/S_m^m)^{1/n} \quad (21)$$

$$S_m = (K_{sp} \Sigma_x^n \Sigma_m^m/S_x^n)^{1/m} \quad (22)$$

equations can be solved provided the total concentration of one of the ions is known, that is S_x or S_m. Assuming a total concentration of one ion the variation in total concentration of the other can be calculated as a function of pH.

Reaction (1) shows that for every mole of $M_m S_n$ which dissolves m moles of M and n moles of X go into solution, hence for the total ion concentrations.

$$S_m = \frac{n}{m} S_x \tag{23}$$

$$S_x = \frac{m}{n} S_m \tag{24}$$

Substituting $\frac{n}{m} S_x$ for S_m in (20)

$$K_{sp} = \frac{(n)^m}{m} S_x^{n + m/n\ m} \tag{25}$$

and

$$S_x = \left[\frac{(m)^m}{n} K_{sp} \Sigma_x^n \Sigma_m^m\right]^{1/m + n} \tag{26}$$

similarly

$$S_m = \left[\frac{(n)^n}{m} K_{sp} \Sigma_x^n \Sigma_m^m\right]^{1/m + n} \tag{27}$$

Equations (26) and (27) relates total concentration of the central atom of the anion and cation to pH through the function Σ_x and Σ_m. Equations (26) and (27) also relates the solubility to solvolysis of both anion and cation.

Radium arsenate, $Ra_3(AsO_4)_2$, dissociates in an aqueous solution according to equation (28) forming the ions Ra(II) and AsO_4(III). The concentration of radium

$$Ra_3 (AsO_4)_2 = 3Ra^{+2} + 2AsO_4^{-3} \tag{28}$$

in solution according to equation 27 is expressed as

$$[Ra^{+2}] = [\frac{(2)^2}{3} \quad K_{sp} \; \Sigma^3_{ASO_4} \; \Sigma^2_{ASO_4} \; \Sigma^2_{RA}]^{1/5} \qquad (27a)$$

Assuming that radium ion does not react with the solvent water at pH's of ground waters then

$$\Sigma^{\;2}_{Ra} = 1$$

and equation 27a reduces to equation 27b.

$$[Ra^{+2}] = [4/3 \; K_{sp} \; \Sigma^3_{ASO_4}]^{1/5} \qquad (27b)$$

Equation 27b states that dissolution of radium arsenate is a function of the degree of hydrolysis of the anion arsenate, hence as the extent of arsenate hydrolysis increases with decreasing pH the solubility of radium arsenate will increase with decreasing pH.

ARSENIC ACID SPECIES AS A FUNCTION OF pH

Arsenic acid is a triprotonic acid, that is it dissociates in three steps. The stepwise dissociation is given by reaction 28, 29 and 30 and the corresponding equilibrium by equations K_{a1}, K_{a2} and K_{a3}. The fraction of

$$H_3AsO_4 = H^+ + H_2AsO_4^- \qquad K_{a1} = \frac{[H_2AsO_4^-][H^+]}{[H_3AsO_4]} = 5.5 \times 10^{-3} \qquad (29)$$

$$H_2AsO_4^- = H^+ + HAsO_4^{=} \qquad K_{a2} = \frac{[HAsO_4^{=}][H^+]}{[H_2AsO_4^-]} = 1.7 \times 10^{-7} \qquad (30)$$

$$HAsO_4^{=} = H^+ + AsO_4^{\equiv} \qquad K_{a3} = \frac{[AsO_4^{\equiv}][H^+]}{[HAsO_4^{=}]} = 3.95 \times 10^{-12} \qquad (31)$$

total arsenic concentration of each moiety as a function of pH were calculated using a mass balance equation, where C is the total concentration and

$$C = [H_3AsO_4] + [H_2AsO_4^-] + [H_2AsO_4^{-2}] + [AsO_4^{-3}] \qquad (32)$$

the relation that the sum of the fractional concentrations equals 1.

$$\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 = 1 \qquad (33)$$

Since the concentration of each individual species can then be expressed in terms of total arsenic concentration, equations for the

$$[H_3AsO_4] = \alpha_0 C,\ [H_2AsO_4^-] = \alpha_1 c,\ [HAsO_4^{=}] = \alpha_2 C,\ [AsO_4] = \alpha_3 C \qquad (34)$$

fractions α_0, α_1, α_2 and α_3 can be derived in terms of hydrogen ion concentration and the equilibrium constants K_{a1}, K_{a2}, K_{a3}. Solutions to these

$$\alpha_0 = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \qquad (35)$$

$$\alpha_1 = \frac{K_{a1}[H+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}\,K_{a2}\,[H^+] + K_{a1}\,K_{a2}\,K_{a3}} \quad (36)$$

$$\alpha_2 = \frac{K_{a1}\,K_{a2}\,[H^+]}{[H^+]^3 + K_a[H^+]^2 + K_{a1}\,K_{a2}\,[H^+] + K_{a1}\,K_{a2}\,K_{a3}} \quad (37)$$

$$\alpha_3 = \frac{K_{a1}\,K_{a2}\,K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}\,K_{a2}\,[H^+] + K_{a1}\,K_{a2}\,K_{a3}} \quad (38)$$

equations are plotted in Figure 1. These plots show the predominant arsenic species in various pH ranges. Thus, it is expected that the type of salt formed by the reaction of a metal ion with arsenate is pH dependent. Radium is thus expected to form the salts $Ra\ (H_2AsO_4)_2$ in the pH range of 2 to 7, $Ra_2\ (H_2AsO_4)_2.HAsO_4$ at a pH of 7, $RaHAsO_4$ in the pH range of 7 to 11.5 and $Ra_3(AsO_4)_2$ at pH's greater than 11.5 These ranges of pH are given without consideration of differences in solubilities.

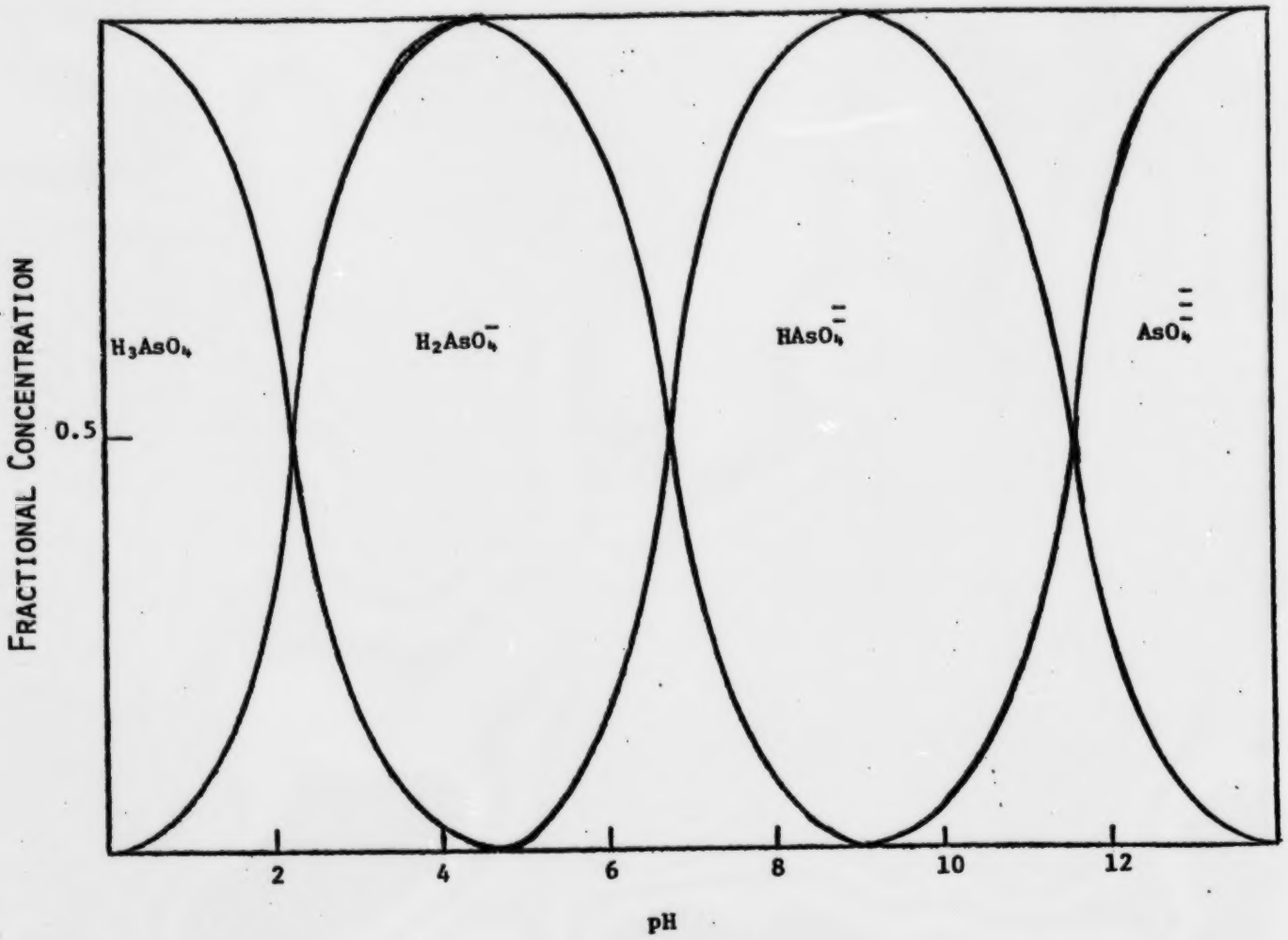

FIGURE 1

DISTRIBUTION OF VARIOUS ARSENATE SPECIES AS A FUNCTION OF pH

CO-PRECIPITATION OF RADIUM

The present practice of decreasing the concentration of radium in uranium mill effluents is by coprecipitation with barium as the sulfates. The reactions and the solubility products of the precipitates are given in equations 39 and 40.

$$Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4 \quad [Ba^{+2}][SO_4^{-2}] = 1.1 \times 10^{-10} \qquad (39)$$

$$Ra^{+2} + SO_4^{-2} \rightarrow RaSO_4 \quad [Ra^{+2}][SO_4^{-2}] = 4.2 \times 10^{-11} \qquad (40)$$

The ratio of their solubility products, $[Ba^{+2}]/[Ra^{+2}]_1$ is 10, i.e. radium in a solution in the presence of solid barium and radium sulfate will be one tenth the concentration of barium. Sulfate concentration is independent of pH at pH's greater than 2 and the reactions of barium and radium have the same stoichiometry, hence the ratio $[Ba^{+2}]/[Ra^{+2}]$ in solution is independent of pH.

Coprecipitation of radium as the arsenate differs from coprecipitation as the sulfate, as the form of the arsenate anion has a greater dependency on pH. Sulfate, at a pH greater than 2.2 exists only as the deprotonated anion $SO_4^{=}$ whereas arsenate exists as $H_2AsO_4^{-}$ from a pH of 2. to 7, $HAsO_4^{=}$ from pH of 7 to 11.5. The deprotonated arsenate $AsO_4^{=}$ is the predominant species only at pH's greater than 11.5. Hence arsenate is available to form various salts with radium depending on the pH whereas sulfate forms only one salt at pH's greater than 2.2. The cations of barium, copper, lead and ferric iron would behave in the same way as radium. Thus a knowledge of the nature of the various precipitates found with arsenate as a function of pH could be beneficial in understanding the coprecipitation of radium.

The solubilities of the precipitates as a

function of pH would also be an influence on coprecipitation as well as column adsorption of radium. It is expected that the greater the solubility of the coprecipitant, the higher the concentration of arsenate, hence decreasing the concentration of radium.

Reactions in which the stoichiometries are not the same are the precipitations of ferric iron (39a) and barium (40a) with arsenate. These reactions are depicted

$$Fe^{+++} + AsO_4^{'''} = FeAsO_4 \qquad [Fe^{+++}]\,[AsO_4^{'''}] = 10^{-21} \qquad (39a)$$

$$3Ba^{++} + 2AsO_4^{'''} = Ba_3(AsO_4)_2 \qquad [Ba^{+2}]^3\,[AsO_4^{'''}]^2 = 10^{-51} \qquad (40a)$$

with their corresponding solubility products by equations 39a and 40a. The ratio $[Fe^{+3}]/[Ba^{+2}]$ is given by equation 41. Since the concentration of arsenate

$$\frac{[Fe^{+3}]}{[Ba^{+2}]} = \frac{K_{sp}^{Fe}}{(K_{sp}^{Ba})^{1/3}} \cdot [AsO_4^{'''}]^{1/3} \qquad (41)$$

is pH dependent the ratio of ferric ion to barium ion is pH dependent.

Equations 39a and 40a not only relate the metal ion concentration to the concentration of arsenate, but as the arsenate concentration is pH dependent the extent of solubility of the metal arsenates is pH dependent. Thus as the power of the arsenate concentration in the two equations are different their variation in concentration with pH will be different i.e. the slopes of cation concentration with pH will be different.

Since plots of cation concentrations of the arsenates of barium and ferric iron as functions of pH have different slopes, they must bisect at a pH where their concentration ratio equals 1. Hence equation 41

can be rearranged to give the concentration of arsenate at this point, i.e. equation 42.

$$[AsO'''_4]^{1/3} = \frac{(K^{Ba}_{sp})^{1/3}}{K^{Fe}_{Sp}} \qquad (42)$$

Substituting the solubility products and solving, the $[AsO'''_4]$ is found to be 4.4×10^{-14} which corresponds to a pH of 4.6 in a system in which the total arsenic concentration is 10^{-4} molar. The concentration of iron and barium will thus be 10^{-4} molar. It is expected that if radium is substituted for barium the radium concentration will be around $10^{-4} - 10^{-5}$ molar.

Since the concentration of arsenate (AsO_4^{-3}) increases with an increase in pH the concentration of radium should decrease with increasing pH. At a pH of 10 the concentration of radium should be in the vicinity of 10^{-9} moles per litre. In the presence of a more soluble arsenate such as copper, lead or ferric iron the solubility of radium would be depressed further.

Coprecipitation, i.e. the entrapment of radium at low concentration by a macroprecipitate, would further depress the concentration of radium.

Experimental Objectives

Knowledge of the chemistry of radium is meager compared to other naturally occurring elements. This lack of knowledge can be attributed to its low concentration in nature as well as its radioactivity. Radium's radioactivity makes it difficult to handle and necessitates taking special precautions. Indications of radium chemistry can be obtained by studying the chemistry of elements of similar ionic charge and especially those elements in the same group of the periodic table, i.e. barium in group 11A of the periodic table.

On the other hand, the chemistry of arsenic as arsenate is quite extensive although solubility products are tabulated only for the metal salts of the deprotonated arsenate species. The predominant arsenate species which is present in aqueous solution is determined by the pH of the solution as depicted in Figure 1, hence the formation of different arsenate-metal ion compositions should be possible by changing the pH of reaction. Studies of these reactions are necessary so as to know what compound is prepared for column absorption of radium as well as which compound is formed by coprecipitation. Such studies involve analysis of precipitates, solubilities and order of mixing reagents.

Provincial environmental standards requires effluent waters contain a maximum of 3 picocurie of radium. This corresponds to 1.3×10^{-14} moles/litre. To reach the low concentration of 3 picocuries the required solubility products, which depends on ratio of anion and cation in the resulting product, are given in the following table:

TABLE 1

STOICHIOMETRY AND REQUIRED SOLUBILITY PRODUCTS FOR SOLUBILITY OF 1 pCi/L RADIUM

Formulae	Ksp
MX	1.9×10^{-29}
MX	3.4×10^{-43}
M_2S_3	1.8×10^{-70}

The usual method of removing radium from solution is to precipitate as the sulfate in the presence of barium. The solubility product of these sulfates are 4.2×10^{-11} and 1.1×10^{-10} respectively. The solubility product of radium sulfate is greater than 1.9×10^{-29} which is required to reduce soluble radium to 1 pCi/L as an MX type salt. The solubility product of radium sulfate allows 6.5×10^{-6} moles of radium i.e. 1.47 ppm to be in solution at equilibrium in which there is no excess of sulfate ion. The environmental requirements call for a concentration of 10^{-9} ppm radium, to reach this concentration as the sulfate the concentration of sulfate must be 10^{4} molar which is an impossibility.

Since the solubility products of barium and radium sulfate are comparable the solubility products of their arsenates should also be comparable, i.e. in the region of 10^{-53}. The objective is thus to determine the conditions which, arsenate plus a coprecipitant, reduces radium concentration in uranium mill effluents to 3 picocurie per litre.

EXPERIMENTAL

Preparation of Solutions

Salt solutions were prepared by dissolving in water weighed amounts of the salt in a volumetric flask and diluting to the mark. The solutions were transferred to storage bottles for future use. The more dilute solutions were prepared by dilution of aliquots of the strong solutions.

Radium solutions were prepared by dilution of 0.00054 mCi of radium -226 in 13.5 L of distilled water. This solution was stored and used as a stock solution for preparation of the radium solutions used throughout these experiments.

Coprecipitation

In a 1000 mL volumetric flask 25 mL of radium stock solution (49.6 pCi/mL) was diluted to the mark with distilled water. 200 mL aliquots of the dilute solution were transferred to 600 mL beakers and pH adjusted to 6. Metal ion was added to individual aliquots so as to have radium solutions containing 0.01, 0.1 and 0.2 mmoles of metal ion. To each sample was added arsenate solution so as to have twice the molar concentration of metal ion, thus to 0.01 mmoles of metal was added 0.02 mmoles of arsenate, to 0.2 mmoles of metal was added 0.4 mmoles of arsenate, etcetera. After addition of arsenate the pH of the solutions were adjusted to 6 and the precipitate filtered using Whatman No. 42 filter paper. The filtrate was evaporated to approximately 5 mL and stored for radium analysis.

The precipitates were split into two portions, one was dried at 110°C and retained for analysis as to composition. The second portion of precipitate was washed with KCl. The resulting wash liquor was evaporated to approximately 5 mL and stored for radium analysis.

The above coprecipitation experiments were repeated in which the radium solution was 1M in Na_2SO_4 and the quantity of metal ions were 0.1, 0.2, 2 and 20 mmoles per 200 mL of solution. The arsenate quantities were 0.2, 0.4, and 40 mmoles. All other conditions were the same as in the previous experiment.

An experiment was also carried out in which the order of addition was reversed i.e., metal ion was added to the radium solution containing arsenate. This experiment was carried out in solutions containing 20 mmoles of metal ion.

ANALYSIS OF PRECIPITATES

The precipitates from the solutions containing 200 mmoles of metal ion were analyzed for metal ion. Techniques employed were X-ray fluorescence and atomic adsorption.

X-RAY FLUORESCENCE

The apparatus consisted of a North American Philips Co. Inc. X-ray spectrograph with a chromium target X-ray tube and a lithium fluoride analyzing crystal. The X-ray tube was operated at 40 KV and 20 ma. An argon-filled Geiger tube was used as a detector.

Pellets consisting of weighed amounts of metal salts were used as the standards for the preparation of working curves. The compounds used were arsenious oxide, ferric oxide, barium carbonate, copper oxide and lead carbonate. The fluorescence data was obtained for specific lines and the quantity of the element present obtained by comparison of the line intensity of sample to a standard curve.

Filtrates were analyzed by irradiation of 3 mL of samples for 20 seconds in liquid sample holders. Concentrations were determined from standard curves obtained by measuring the fluorescence intensity of standard solutions.

ATOMIC ABSORPTION

The apparatus consisted of a Perkin Elmer Model 560 Atomic Absorption Spectrometer. Aliquots of filtrate were diluted with acid to give a known volume of solution 10% in HCl. The absorbance of the filtrate samples were compared with absorbance of standards to obtain metal ion concentration. The standards consisted of known concentrations of metal ions in 10% HCl solution.

COPPER AND LEAD BY SPECIFIC ION ELECTRODES

Standard solutions of 0.1M copper and lead were prepared from copper foil and lead oxide. Solutions 10^{-3}, 10^{-4} and 10^{-5} molar of the metal ions were prepared by serial dilution of the 0.1 M solutions. Concentrations of copper and lead in solutions were determined by comparison of electrode potentials with the electrode potentials of standard solutions.

SOLUBILITIES OF COPPER AND LEAD ARSENATES

Precipitates from coprecipitation experiments were washed with distilled water and dried at 110^{0}C. The dried precipitates were added to 100 mL of distilled water and the pH adjusted with dilute HNO_3 or NaOH. The metal ion concentration was determined using specific ion electrodes. Concentration of metal ions were determined over pH range of 3 to 11.

PREPARATION OF ADSORBENTS

There are a number of products on the market which are used for adsorbing oils and water. These products are different in adsorption capacity, hence they will form exchange type products of different capacity. The adsorbance of different commercial products are:

TABLE 3

ABSORBANCE OF DIATOMITE PRODUCTS

Product	Absorbance Wt %
Floor Dry	119
Poise	100
Cats Pride	85
Kitty Kleen	66

Two products are to be tested as supports of metal arsenates, Floor Dry, a product imported from the United States and Kitty Kleen, a Nova Scotia product.

EXPERIMENTAL ABSORPTION CAPACITY

By Volume:

Samples of 100 mL of each brand were measured into 250 mL beakers. Water was steadily poured into the samples and allowed to stand for 15 seconds. The excess water was drained, measured and subtracted from the total volume giving the volume and per cent adsorbed by the sample.

By Weight:

Absorption by product weight was performed as described for the *by volume* test except the sample was weighed before and after addition of water.

IMPREGNATION OF ABSORBANT WITH METAL ARSENATES

Preparation of Solutions:

Solutions of the metal ions were prepared by dissolving a weighed portion of metal salt in 1 litre of distilled water. The salts and weights used to prepare 4% Wt/Volume solutions are given in Table 3. The $Na_2HAsO_4.7H_2O$ solution was 4% as $HAsO_4$.

TABLE 3

REAGENT SOLUTION COMPOSITION

Reagent	Wt/L, g	Molarity
$BaCl_2.2H_2O$	71.14	0.29
$CuCl_2.2H_2O$	107.3	0.63
$FeCl_3.6H_2O$	193.6	0.72
$Pb(C_2H_3O_2)_2.3H_2O$	73.23	0.19
$Na_2HAsO_4.7H_2O$	89.2	0.29

IMPREGNATION OF ABSORBANT

The volume of reagents used in preparing absorbants was based on the absorbance capacity of the absorbant, i.e., the total volume of reagents added was equal to or less than the absorbant capacity.

Five hundred mL of absorbant is transferred to a 2L beaker. The solution of the metal ion is slowly added to the absorbant with continuous stirring. Stirring is continued after all the metal ion solution is added until a homogeneous mix is obtained. The solution of $NaHAsO_4.7H_2O$ is then added with stirring and continued to obtain a homogeneous mix. The mixture is then washed with distilled water until free of fines and stored for future testing.

The volumes of reagents used in preparing these absorbants are given in Table 4.

TABLE 4

VOLUME OF REAGENTS USED IN PREPARING ABSORBANTS

Reagent	Volume Metal Salt Solution	Volume Na_2HAsO_4 Solution	pH
$BaCl_2.2H_2O$	165 mL	110 mL	7.6
$CuCl_2.2H_2O$	65 mL	210 mL	6.7
$FeCl_3.6H_2O$	79 mL	196 mL	4.4
$Pb(C_2H_3O_2)_2.3H_2O$	109 mL	166 mL	7.3

RESULTS AND DISCUSSION

Metal Arsenates

Arsenates of barium, copper, lead and iron were precipitated from solution at various pHs, dried at 110°C, and analyzed by X-ray fluorescence and X-ray diffraction. X-ray diffraction showed all arsenates of barium, copper, lead and iron to be amorphous regardless of pH at which they were formed.

The per cent arsenic in the precipitates were determined by X-ray fluorescence and the values obtained were compared with per cent arsenic of assumed compound composition. The suggested formulae and pH at which they formed are given in Table 5. Barium forms a double salt at pH of 7 as at this pH arsenate is present as the mono- and di-protonated anions.

The composition of the salts formed are pH dependent as pH controls the form of the anion and cation which enters into the reaction. Consider the reaction of ferric iron with arsenate at pH of 4. Ferric iron is present in aqueous solution as $Fe(OH)_2\ (H_2O)_4^+$ and arsenate as $H_2AsO_4^-$. Thus the reaction is:

$$Fe(OH)_2\ (H_2O)_4^+ + H_2AsO_4^- = FeAsO_4.2H_2O$$

The reactions of arsenate with lead, copper and barium can be depicted by equations 1 to 4.

$$Pb(OH)^+ + H_2AsO_4^- = PbHAsO_4$$

$$Cu^{+2} + 2Cu(OH)^+ + 2H\ AsO_4 = Cu_3(AsO_4)_2 + 2H_2O$$

$$2Ba^{++} + HAsO_4^{=} + 2H_2AsO_4^- = BaHAsO_4 \cdot Ba(H_2AsO_4)_2$$

A significant point of coprecipitation of radium with barium arsenate in the presence of sulfate at a pH of 6 is the formation of barium sulfate. Barium sulfate formation is indicated by the high percentage of SO_4 in the precipitate. When the molar ratios are calculated from the weight per cent composition the resulting formula is

$$Ba_4(SO_4)_3\ AsO_4$$

which transforms to

$$(BaSO_4)_3.BaHAsO_4$$

when electroneutrality of compounds is considered. The other three metal precipitates do not contain enough sulfate to indicate extensive metal sulfate formation.

Comparison of the methods of analysis of the precipitates indicates that X-ray fluorescence yields unreliable results for copper, lead and ferric iron. In determining copper the results were about 50% higher than the quantity added. In the case of lead and ferric iron the results were less than 50% of the quantity added. Nearly one hundred per cent precipitation of cation is indicated by analysis of the mother liquor for copper, lead and ferric iron by atomic absorption and specific ion electrode. Disagreement in analytical results for the precipitates of copper, lead and ferric iron precludes commenting on the nature of these precipitates even though atomic absorption shows approximately complete precipitation of the metals.

TABLE 5

ARSENATE COMPOUNDS FORMED BY PRECIPITATION FROM SOLUTION

COMPOUND	pH OF PRECIPITATION	SOLUBILITY ppm As (pH range)
$Cu_5As_4O_{15}.10H_2O$	3	
$Cu_3(AsO_{4-2}.6H_2O$	7	7 - 10 (10 - 5)
$Cu_3(AsO_4)\ (OH)_3$	10.5	
$BaHAsO_4.Ba(H_2AsO_4)_2$	7	155 - 190 (6.8 - 10)
$Ba_3(AsO_4)_2$	10.5	
$Pb_5(AsO_4)_3Cl$	6	0.08 - 0.11 (4 - 10)
$Pb\ HAsO_4$	10.5	
$Pb\ HAsO_4$*	10.5	
$FeAsO_4$	4	
$Th_3(AsO_4)_4$	2	0.5 - 0.3 (4.2 - 9.6)

* - Prepared from lead acetate

It is evident that to prepare the various arsenates of the general formula $M_3(AsO_4)_2$ attention must be given to pH. Thus copper forms a mixed salt with arsenate in an acid medium and the desired compound $Cu_3(AsO_4)_2$ in a neutral solution. In an alkaline medium copper forms a hydroxy arsenate. To form the arsenates of barium and lead a pH of 10.5 and a pH greater than 10.5 respectively is required.

SOLUBILITIES

Solubility studies were carried out on copper and lead arsenates in which the precipitates were formed by three different methods. The concentrations of metal ions were determined using specific ion electrodes. The results at various pHs are recorded in Table 6.

TABLE 6

SOLUBILITIES OF COPPER AND LEAD ARSENATES AS FUNCTIONS OF pH

pH	Cu ppm			Pb ppm		
	#4	M-2	CC14	M-4	CP14	CP15
3	5	4.5	4.2			
4	1	0.8	0.62	10	4	7
5	1	0.48	0.31	7.6	0.85	0.92
6	0.21	0.72	0.11	0.66	0.52	0.41
7	0.12	0.05	0.06	0.06	0.84	0.21
8	.04	0.02	0.03	0.04	0.11	0.15
9	0.001	<0.001	<0.001	0.01	0.05	0.07
10	<0.001	<0.001	<0.001	<0.01	<0.01	<0.01
11	<0.001	<0.001	<0.001			

#4 - Copper arsenate prepared by addition of arsenate solution to copper chloride solution at pH of 7.

M-4 - Lead arsenate prepared by addition of lead solution to arsenate solution at a pH of 12.3.

M-2 - Copper arsenate prepared by addition of copper chloride solution to arsenate solution at a pH of 11.

CC14 and CP 14 were prepared in a 1M Na_2SO_4 solution by addition of arsenate to metal solution at pH 6.

CP 15 was prepared in a 1 M Na_2SO_4 arsenate solution at pH 6 by addition of lead salt solution.

It is to be noted that the solubilities increase with decreasing pH as would be predicted from equation 27.

YIELD OF PRECIPITATES

The effect of order of addition of reagents was investigated by comparing the yield of precipitates for the two orders of mixing. The results are recorded in Table 7. The difference in the quantity of precipitate formed by the two methods is insignificant, i.e., the order of addition of reagents does not influence the quantity of precipitate formed.

TABLE 7

PRECIPITATE YIELD AND ORDER OF ADDITION OF REAGENTS

40 mmoles of Arsenate reacted with 20 mmoles of cation at pH 6.

Cation	g of Precipitate	
	Anion to Cation	Cation to Anion
Ba	5.1 g	5.2
Cu	4.1	4.3
Pb	7.0	7.3
Fe	7.9	7.3

The concentration of metal in solution of all samples decreased with increasing pH. It is assumed that the concentration of the arsenate moiety also decreases in concentration with increasing pH. It is expected, since radium is divalent as is copper and lead, that the

solubility of radium arsenate will decrease with increasng pH, hence the higher the pH of radium containing solutions the more efficient will be the removal of radium as the arsenate by column absorption and by coprecipitation.

ABSORBANTS

Absorbants were prepared by impregnating both Kitty Kleen (kitty litter) and Floor Dry 85 (an oil absorbant) with metal arsenates. The resulting products were analyzed for metal retained on the absorbant the values of which are given in Table 8. It is evident that Floor Dry retains the largest quantity of metal arsenate. The increase in retention by Floor Dry 85 of copper arsenate, ferric arsenate and lead arsenate is 2X, 5X and 7X respectively over the retention by Kitty Kleen. This increase in retention by Floor Dry is due to its greater absorbance capacity as given in Table 2.

Order of addition of reactants also has an effect on amount of metal arsenate retained by the support material. When arsenate is added to the metal ion absorbed by Floor Dry there is a 2 to 4 fold increase in quantity of metal ion adhering to the support. The products prepared by the addition of arsenate to the metal ion are to be tested as ion exchangers for removal of radium from solution.

TABLE 8

ANALYSIS OF PREPARED ABSORBANTS

REAGENT	KITTY KLEEN	F L O O R	D R Y	
	Metal Ion	Metal Ion	Metal Ion	Arsenic*
$BaCl_2.2H_2O$			0.48%	0.56%
$CuCl_2.2H_2O$	0.23%	0.48	0.85	0.28
$FeCl_3.6H_2O$	0.27	1.21	2.28	0.89
$Pb(C_2H_2O_2).3H_2O$	0.06	0.39	1.46	0.45

* - Absorbants prepared by adding the arsenate to the metal ion on absorbant; others prepared by adding the metal ion to the arsenate on the absorbant.

COLUMN ABSORPTION OF RADIUM

The efficiency of ion exchange is dependent on the nature of the solution as well as the contact time between the solution and ion exchanger. The nature of solutes in aqueous solution are determined primarily by pH. This is demonstrated in Figure 1 in which the various species of arsenic acid are shown as functions of pH. Similar relationships can be shown for ferric ion which forms $Fe(H_2O)_6^{+3}$, $Fe(H_2O)_5(OH)^{+2}$ and $Fe(H_2O)_4(OH)_2^{+}$ by changing the pH of solution from 1 to 7. As the pH is changed the species of complexed ferric ion which is predominant changes.

The formation of complex ions between radium and hydroxyl radicals is unknown i.e. $Ra(OH)^{+}$. Hence all reactions of radium in solution are considered as occurring with the radium ion Ra^{+2}. Thus at various pH's radium can be considered as reacting with arsenate according to the following equations.

pH2-7

$$Ra^{+2} + 2\ H_2AsO_4^{-} = Ra(H_2AsO_4)_2$$

pH7-10.5

$$Ra^{+2} + HAsO_4^{=} = RaHAsO_4$$

pH10.5 +

$$3Ra^{+2} + 2AsO_4^{=} = Ra_3(AsO_4)_2$$

The suggested products of these reactions compare favorably with the results obtained with barium and arsenate given in Table 4.

Flow rate can have a marked effect on efficiency of ion exchange. Thus as the flow rate increases the contact time between the solution and the exchanger decreases hence not allowing time for the solute to react with the exchanger. The absorption of radium by metal arsenates as ion exchangers is shown in Table 9 at various flow rates. On the basis of per cent radium removed the differences are small for copper, iron and lead arsenates. Flow rate has an effect on the efficiency of barium arsenate in removing radium from solution as flow rate increases the quantity of radium removed from solution decreases. The decrease in efficiency of barium arsenate compared to the other three metal arsenates can be ascribed to the greater insolubility of barium arsenate. Barium arsenate has a solubility product of 8×10^{-51} whereas copper, ferric iron and lead arsenates have solubility products of 4.7×10^{-21} and 4×10^{-36} respectively. These larger solubility products show that larger concentrations of arsenate in the vicinity of the exchanger particles hence faster is the reaction between arsenate and radium. The faster the reaction the less contact time required for removal of radium hence larger flow rates are possible.

It has been shown in Table 6 that pH has an effect on solubility of metal arsenates, that is as the pH increases solubility decreases. pH has also been shown to determine the nature of the products of reaction, thus arsenates as AsO_4 are least soluble, hence it is expected that pH will have an effect on the column absorption of radium. Table 10 shows the effect of pH on the absorption of radium by the four different metal arsenates. The overall conclusion is that as the pH increases the absorption of radium increases due to decreases in solubility of radium arsenate.

TABLE 9

FLOW RATE AND
COLUMN ABSORPTION OF RADIUM

COLUMN	FLOW RATE mL/min	COUNTS EFFLUENT Ra, 1000 sec.	% Ra ABSORBED
Ba	7.27	8	99.7
	23.1	24	98.7
	44.4	79	95.8
Cu	5.83	15	99.2
	22.8	21	98.9
	37.5	13	99.3
Fe	6.61	12	99.4
	30.5	11	99.4
	45.6	15	99.2
Pb	6.23	9	99.5
	26.1	10	99.5
	40.0	12	99.4

Influent - 1898 counts Ra-226 for 1000 sec.

Background - 0 counts

pH - 5.6

Void volume - 12 mL

TABLE 10

EFFECT OF pH ON COLUMN ABSORPTION OF RADIUM

CATION	pH	FLOW RATE	% Ra ABSORBED
Ba	4	27.8	92.1*
	5.6	23.1	99.2
	8.0	32.3	98.3
	10.0	40.0	99.0
Cu	4.	22.7	99.6
	5.6	22.7	99.4
	8.0	29.0	99.7
	10.0	29.9	99.9
Pb	4	24.8	98.2*
	5.6	26.3	99.9
	8.0	26.3	99.8
	10.0	31.7	100.
Fe	4.0	24.8	98.2*
	5.6	26.3	99.9
	8.0	26.3	99.8
	10.0	31.7	100.0

COPRECIPITATION OF RADIUM

The initial experiments on the coprecipitation of radium with metal arsenates were designed to determine the minimum quantity of metal arsenates necessary for maximum precipitation of the radium. The results of these experiments are tabulated in Table 11 and show that at least 2 mmoles of the macro component is necessary to treat 200 mLs of radium solution. This quantity removes a minimum of 99% of the radium. It is also evident that at low concentrations of the macro ion the quantity of radium removed from solution is dependent on the metal used as the macro ion.

The efficiency of barium arsenate in coprecipitating radium arsenate is primarily due to similarity in ionic size, Ba^{+2} 1.43 Å and Ra^{+2} 1.52 Å. Similarity in size allows inclusion of radium in the barium arsenate precipitate without too much distortion or structural deformation. The extent of structural deformation can be expected to increase as the size of the macro ion decreases with a corresponding decrease in extent of coprecipitation. This is observed with lead (radii 1.32) and copper (radii ≈0.8). Iron (radii 0.67) is more efficient in coprecipitating radium than lead or copper even though its ionic radii is smaller. This anomaly is unexplainable at this time.

The effect of pH has been shown in Table 5 to influence the species of metal arsenate formed. It is thus expected that pH will influence the coprecipitation of radium. Barium arsenate did not

TABLE 11

COPRECIPITATION OF RADIUM

EFFECT OF QUANTITY OF PRECIPITANT ON EFFICIENCY OF RADIUM REMOVAL

PRECIPITANT	$pCiRa^{226}$ in MOTHER LIQUOR	% REMOVED	QUANTITY, mmoles
Barium	6	97.6	0.1
	3.5	98.6	0.2
	0	100	2.0
Copper	33	88.7	0.1
	3.5	98.6	0.2
	2.5	99.0	2.0
Lead	24	90.3	0.1
	9	96.4	0.2
	2	99.2	2.0
Iron	10.5	95.8	0.1
	2	99.2	0.2
	1	99.6	2.0

^{226}Ra initial - 248 pCi.

pH 6

form a precipitate below a pH of 4 hence it is expected that radium will not form an arsenate below a pH of 4. All other coprecipitations were carried out at pH's greater than 4.

Coprecipitation of radium with ferric arsenate resulted in a marked decrease in radium in solution. Between the pH's of 4 and 8 there remained between 1 and 3 pCi of radium in solution.

The precipitates and mother liquors obtained from coprecipitation experiments were analyzed for composition. The results of these analyses are given in Table 12 for the various precipitants and conditions. These analysis indicates what is occurring during coprecipitation of radium with the various reagents and generally there is essentially complete precipitation of the macro metal ion in an excess of arsenate ion at a pH of 6.

A significant point of coprecipitation of radium with barium arsenate in the presence of sulfate at a pH of 6 is the formation of barium sulfate. Barium sulfate formation is indicated by the high percentage of SO_4 in the precipitate. When the molar ratios are calculated from the weight per cent composition the resulting formula is

$$Ba_4(SO_4)_3AsO_4$$

which transforms to

$$(BaSO_4)_3.BaHAsO_4$$

when electroneutrality of compounds is considered. The other three metal precipitates do not contain enough sulfate to indicate extensive metal sulfate formation.

TABLE 12

RESULTS OF ANALYSIS OF COPRECIPITATES AND FILTRATES

METAL PRECIPITANT	m moles M^{n+} added	Conc. of $SO_4^{=}$ in Ra^{226} Soln.	ANALYSIS OF SOLUTION					ANALYSIS OF PRECIPITATE				
			TOTAL VOLUME (mL)	X-RAY m moles M^{n+}	X-RAY m moles As	A. A. m moles M^{n+}	ION ELECTRODE m moles M^{n+}	TOTAL WEIGHT	X-RAY m moles M^{n+}	X-RAY m moles As	A.A. m moles M^{n+}	X-RAY Wt % SO_4
BARIUM	0.01	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	0	evp	- -	- -	- -	- -	- -	- -	- -	- -	
	0.2	0	evp	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	1.0M	220	0.15	0.29	- -	- -	- -	- -	- -	- -	
	0.2	1.0M	240	0.07	0.48	- -	- -	- -	- -	- -	- -	
	2.0	1.0M	240	0.07	0.48	- -	- -	0.17g	- -	- -	- -	
	20.0	1.0M	270	- -	- -	- -	- -	5.1g	21.(56%)*	4.8 (13%)*	- -	31
	20.0	1.0M	245	- -	- -	- -	- -	5.2g	23.(60%)*	3.0 (8%)*	- -	36
COPPER	0.01	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.2	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	1.0M	220	0	0.23	0.07	0.0014	- -	- -	- -	- -	
	0.2	1.0M	240	0	0.38	0.09	0.0011	- -	- -	- -	- -	
	2.0	1.0M	240	0	2.5	0.002	0.000045	0.42g.	- -	- -	- -	
	20.0	1.0M	288	- -	- -	0.001	<0.00004	4.1g	28.0	5.8	18.0	<1%
	20.0	1.0M	250	- -	- -	0.001	<0.00004	6.3	30.4	8.0	15.0	1.4%
LEAD	0.01	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.2	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	1.0M	220	0	0.42	0.0006	<0.00016	- -	- -	- -	- -	
	0.2	1.0M	240	0	0.43	0.0004	<0.00012	- -	- -	- -	- -	
	2.0	1.0M	240	0	2.2	0.0007	<0.00012	3.6	- -	- -	- -	
	20.0	1.0M	430	- -	- -	0.0005	<0.00021	7.0	7.6	9.3	22.0	< 1%
	20.0	1.0M	315	- -	- -	0.0004	<0.00015	7.3	8.9	6.3	21.0	< 1%
FERRIC IRON	0.01	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.2	0	evp.	- -	- -	- -	- -	- -	- -	- -	- -	
	0.1	1.0M	220	0	0.15	0.0046	- -	- -	- -	- -	- -	
	0.2	1.0M	240	0	0.29	0.0051	- -	- -	- -	- -	- -	
	2.0	1.0M	240	0	3.0	0.019	- -	0.38	- -	- -	- -	
	20.0	1.0M	375	- -	- -	0.513	- -	7.9	7.5	11.0	20.0	2.7%
	20.0	1.0M	232	- -	- -	0.333	- -	7.3	7.3	11.0	18.0	<1%

* - Weight per cent as Ba and AsO_4.

pH 6
Moles ratio Ba:As = 1:2

Comparison of the methods of analysis of the precipitates indicates that X-ray fluorescence yields unreliable results for copper, lead and ferric iron. In determining copper the results were about 50% higher than the quantity added. In the case of lead and ferric iron the results were less than 50% of the quantity added. Nearly one hundred per cent precipitation of cation is indicated by analysis of the mother liquor for copper, lead and ferric iron by atomic absorption and specific ion electrode. Disagreement in analytical results for the precipitates of copper, lead and ferric iron precludes commenting on the nature of these precipitates even though atomic absorption shows approximately complete precipitation of the metals.

The results of analyzing the precipitates of copper, lead and iron for the macro ion and arsenic show indefinite composition. This would be due to the methods of analysis hence the methods need to be studied for this application.

CONCLUSIONS

1. Arsenates of copper and lead increase in solubility with decreasing pH.

2. Barium forms a double salt when barium arsenate precipitated in the presence of sulfate at a pH of 6.

3. The type of metal arsenate formed by the ions of copper, lead and barium is pH dependent.

4. Thorium forms an insoluble arsenate at a pH of 2. This could be useful in removing thorium from uranium mill streams and from plant mill effluents.

5. Ion exchangers can be prepared by depositing metal arsenates on diatomite material.

6. All four exchangers, copper, lead, barium and ferric iron arsenates removed over 99% of radium from solution at a pH of 5.6 to 10.

7. The efficiency of metal arsenates in removing radium from solution increases with increasing pH. This increase in efficiency is probably due to the increase in concentration of the deprotonated arsenate ion.

SUGGESTED FURTHER INVESTIGATION

1. Determine the optimum conditions for the coprecipitation of radium by each macro precipitant.

2. Study the effect of flocculants in enhancing the coprecipitation of radium as an arsenate.

3. Study the removal of thorium from effluents and uranium mill streams as the arsenate by coprecipitation and by column adsorption.

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APPENDIX

DETERMINATION OF RADIUM -226

The determination of Ra-226 consists of counting alpha particles of 4.78 MeV. The instrumentation consisted of a multi-channel analyzer and a surface barrier detector in a vacuum chamber. Planchettes are used to contain the sample for counting.

Liquid samples are prepared for measurement by evaporation, transfer to the planchette followed by evaporation to dryness. The planchette is transferred to the vacuum chamber and placed immediately below surface of the detector. A vacuum is pulled on the detector chamber and the alpha radiation counted. The quantity of radium 226 is determined by reference to standards measured by the same method.

ENERGY CALIBRATION

Spectra from ^{241}Am and ^{226}Ra were collected for the same bias voltage on the detector (130V). The channel number of peak maximum and the energy of the corresponding alpha particles were plotted on graph paper. Three additional peaks were present in the radium spectra which were considered as daughters of radium 226, i.e., radon 222, polonium 218 and polonium 214. These points were also plotted on the graph and used as values in constructing the line relating channel number and particle energy. The resulting plot is given in Figure 1. A straight line relationship exists between channel number and alpha particle energy.

Standard quantities of radium 226 were measured using the same instrumental conditions as for determining the relationship of channel number and particle energy. The resulting counts per minute were plotted against the number of pCi of ^{226}Ra present. A straight line relationship between number of counts and quaznttity was obtained as shown in Figure 2.

FIGURE 1 - ENERGY STANDARDIZATION CURVE FOR α-PARTICLE DETECTOR

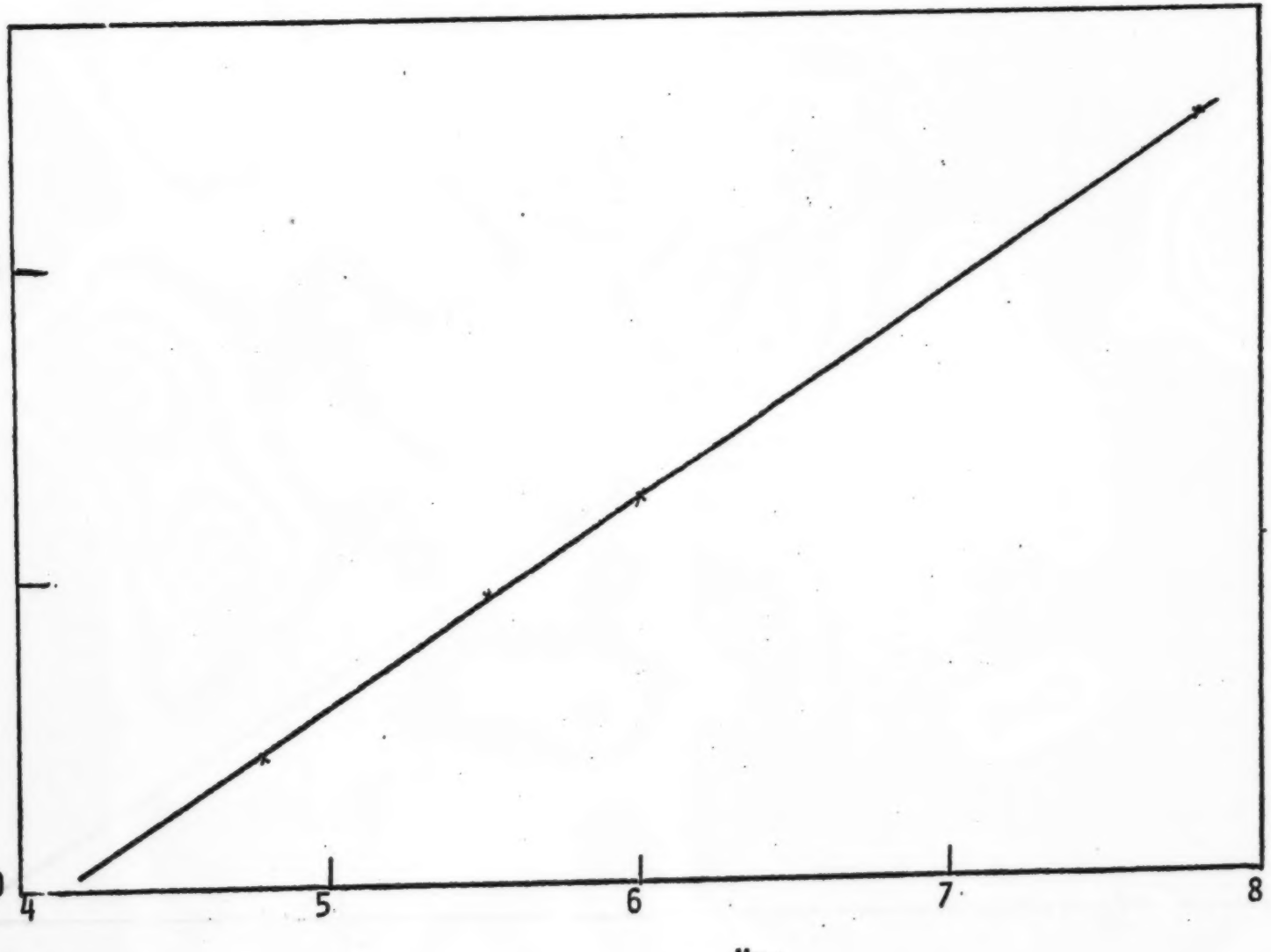

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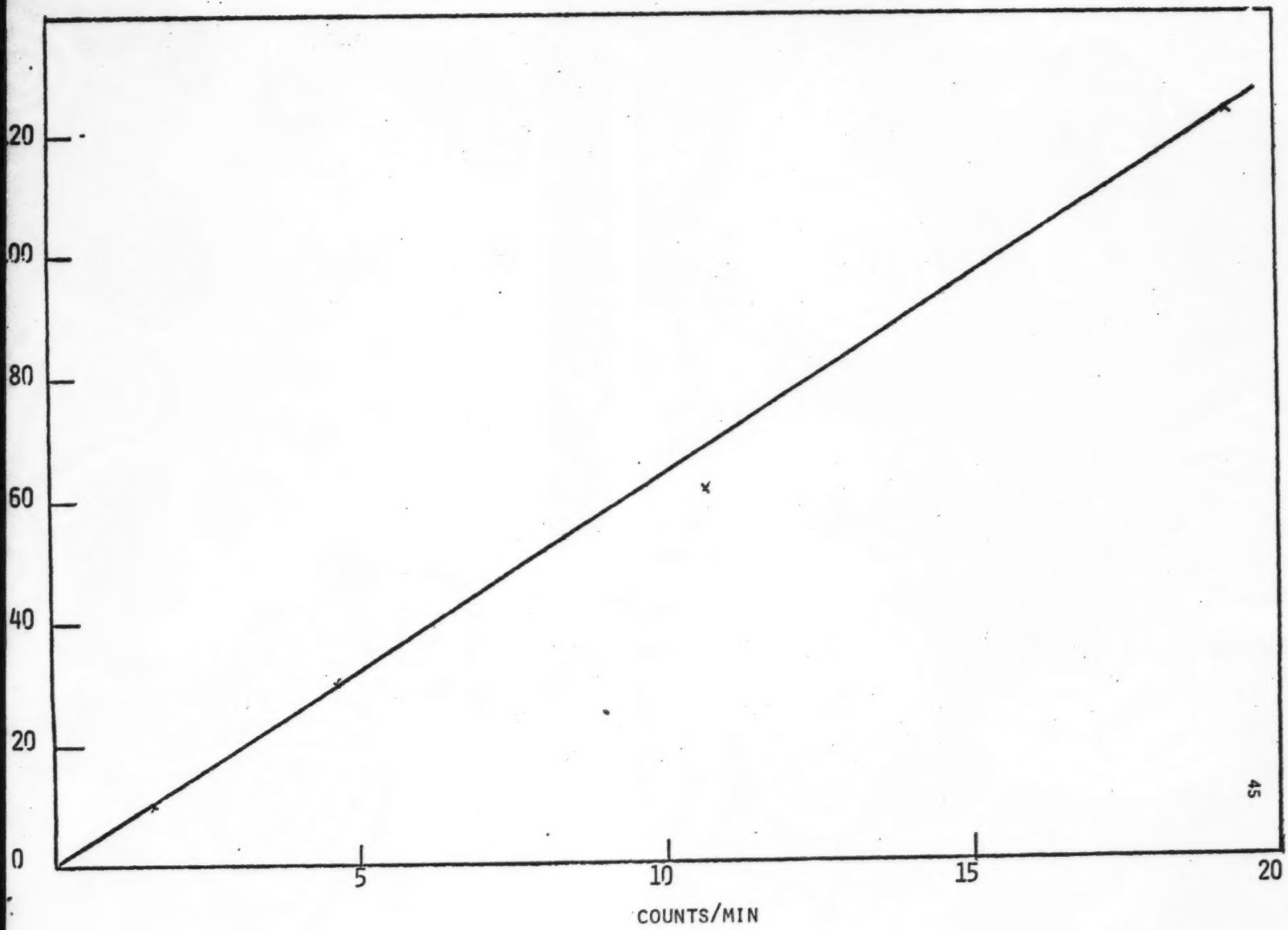
FIGURE 2 - CALIBRATION CURVE FOR RADIUM 226



APPENDIX

DETERMINATION OF RADIUM BY ABSORPTION

Radium is absorbed by the arsenates of ferric iron, barium, copper and lead, hence an analytical application of this reaction is seen as the absorption of radium on a thin layer of metal arsenate and then counting the alpha particles emitted.

This idea was tested by precipitating the metal arsenates on Whatman 2044 Filter paper. Through each metal arsenate was passed 100 ml of solution containing 200 pCi of Ra-226. The filters were then washed with 50 mL of distilled water and dried. The results obtained are summarized in Table 13.

TABLE 13

RADIUM ABSORBED BY THIN LAYERS OF METAL ARSENATES

ARSENATE	% Ra-226 ABSORBED BY
Ba	2.3
Cu	0.8
Fe	8.5
Pb	10.8

It is quite obvious that this technique is not work applicable to radium. The main factor contributing to its failure is probably the very short contact time.